

Total Electron Scattering and Electronic State Excitations Cross Sections for O₂, CO, and CH₄

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Available electron collision cross section data concerning total and elastic scattering, vibrational excitation, and ionization for O₂, CO, and CH₄ have been critically reviewed, and a set of cross sections for modeling of planetary atmospheric behavior is recommended. Utilizing these recommended cross sections, we derived total electronic state excitation cross sections and upper limits for dissociation cross sections, which in the case of CH₄ should very closely equal the actual dissociation cross section.

INTRODUCTION

Electron collision cross sections for momentum transfer, excitation, dissociation, and ionization of the components of planetary atmospheres are needed for the modeling of the behavior of these atmospheres, for interpretation of spectroscopic information and planning of future missions. Although much work has taken place in the area of electron collision physics in the past decades, our knowledge of pertinent cross sections for planetary atmospheric modeling is still very fragmentary. Absolute cross-section measurements are tedious, and difficult procedures and theoretical approaches are not reliable without checks against benchmark experimental data.

The most accurate information is available on total electron scattering cross sections (Q_T). Ionization cross sections (Q_I) are also reasonably well determined for most of the atmospherically important atoms and molecules. The purpose of the present paper is to review and utilize these cross sections in combination with available elastic scattering (Q_{elas}) and vibrational excitation cross sections (Q_v) to obtain total electronic state excitation cross sections (Q_{elec}) for O₂, CO, and CH₄ in the 1 to 1000 eV electron impact energy range. These investigations also yield upper limits on cross sections for electron impact dissociation (Q_D) and in the case of CH₄, this upper limit should correspond to the actual value of Q_D .

All cross sections given in this article are in 10^{-16} cm^2 units unless stated otherwise. We have not used cross sections which were reported only in form of figures or in arbitrary units.

APPROACH

Deduction of total electronic state excitation cross sections is based on the following equation:

$$\sum_n Q'_{\text{elec}}(E) = Q_T(E) - Q_I(E) - Q_{\text{elas}}(E) - Q_v(E) \quad (1)$$

where E refers to the electron impact energy. The other quantities are as defined above. The summation on the left-hand side of (1) is over all (n) electronic states of the molecule. (Rotational excitation has been omitted from the right-hand side of (1) because in the experimental data on Q_{elas} , these cross sections are included.) The best known quantity in (1) is Q_T . It has, in general, been measured with an accuracy of a few percent by several investigators over a wide energy range for all species. Next in line, as far as accuracy and availability of data are concerned, is Q_I . Measurements, sometimes from several laboratories, are available over a wide range of impact energy but the accuracy is in general only of the order of 10%, and deviations considerably larger than this frequently occur in the reported data. Elastic scattering cross sections are not as readily available as Q_T and Q_I . They are obtained from differential scattering experiments over limited (by experimental conditions) angular range by extrapolation and integration of the measured values. Typical error limits for these values are 10 to 20%. Rotational excitation is usually not resolved in these measurements and, as mentioned above, they are included in the Q_{elas} values. Finally, vibrational excitation cross sections are the least known quantities, but fortunately they are small and do not have significant influence in our scheme.

Our procedure is to review all available data and, based on critical (but undeniably somewhat arbitrary) evaluation of these data, come up with a set of recommended cross sections for the right-hand side of (1). This yields us the total electronic state excitation cross sections, which represents the best we can do at the present time. This procedure also allows us to derive some conclusions concerning the cross sections for electron-impact dissociation of molecules to neutral fragments. Unfortunately, very little information is available on this subject, and the measurement of these cross sections is difficult (the major difficulty is associated with the detection of neutral fragments). The $\sum_n Q'_{\text{elec}}(E)$ values represent an upper limit to $Q_D(E)$, in general, but in the case of CH₄ (and other complex molecules),

which predominantly dissociates upon excitation of electronic states, the two values become identical.

RECOMMENDED CROSS SECTIONS

Oxygen

Total electron scattering cross sections for O_2 are available from *Sunshine et al.* [1967], *Dalba et al.* [1980], *Zecca et al.* [1986], *Dababneh et al.* [1988], *Subramanian and Kumar* [1990] and *Kanik et al.* [1992a]. These results as well as the recommended values are shown in Figure 1. At impact energies above 5 eV, the reported cross sections are in agreement within the stated error limits except those of *Sunshine et al.* [1967] and *Dababneh et al.* [1988]. Below 5 eV there is considerable scatter in the reported values.

Integral elastic cross sections have been deduced from available total and inelastic cross sections by *Trajmar et al.* [1971] and from differential cross sections (DCS) by *Trajmar et al.* [1972], *Shyn and Sharp* [1982] and *Iga et al.* [1987] (Figure 2). *Diamon et al.* [1982] measured relative elastic DCS in the 4 - 140° angular range at 200, 300, 400, and 500 eV impact energies and normalized these cross sections to the absolute measurement of *Bromberg* [1974] at 500 eV in the 2 to 40° angular range. We extrapolated and integrated the DCS reported by *Diamon et al.* [1982]. These cross sections and recommended values below 50 eV are smaller than those of *Shyn and Sharp* [1982]. We recommend these lower values because the elastic cross sections of *Shyn and Sharp* [1982] below 10 eV are larger than the Q_T values and we trust these later cross sections more. At 200 eV there is a significant mismatch between the curve representing the *Shyn and Sharp* [1982] results and the curve representing the high-energy results of *Diamon et al.* [1982] and *Iga et al.* [1987]. We drew the curve for our recommended values between the two curves, representing the reported values as a compromise.

Total ionization cross sections have been measured by *Craggs et al.* [1957], *Asundi et al.* [1963], *Schram et al.* [1965], *Rapp and Englander-Golden* [1965], *Peresse and Tuffin* [1967] and *Krishnakumar and Srivastava* [1992]. We accepted the results of *Krishnakumar and Srivastava* in the threshold to 1000 eV range as our recommended cross sections. The cross sections reported by *Schram et al.* [1965] are about 12% lower in the overlapping (600 to 1000 eV) region but they should serve as good guides in the 1000 to 20,000 eV region. These results are shown in Figure 3.

No vibrational excitation cross sections are available for O_2 .

In Figure 4 we show the $\Sigma(Q_{elec}^n + Q_v)$ values obtained from (1) as well as previous estimations of these values from *Trajmar et al.* [1971, 1972]. The recommended values are given by the dot-dash line.

A summary of all recommended cross sections is given in Table 1 and shown in Figure 5.

Carbon monoxide

Q_T results have been reported by *Kwan et al.* [1983], *Buckman and Lohmann* [1986], *Garcia et al.* [1990] and *Kanik et al.* [1992a]. In the impact energy region of 2 to 1000 eV the reported values are in good agreement. Below 2 eV the results of *Kwan et al.* [1983] and *Buckman and Lohmann* [1986] differ significantly. We recommend the more recent values given by *Buckman and Lohmann*. Above 500 eV, Q_T values are available only from *Garcia et al.* [1990] and these values merge smoothly with the recommended values at lower energies. The Q_T results and recommended values are shown in Figure 6.

Differential, elastic scattering cross sections have been reported by *Bromberg* [1969, 1970] at 300, 400, and 500 eV, *Du Bois and Rudd* [1976] at 200, 500, and 800 eV, and *Tanaka et al.* [1978] in the 3 to 1000 eV range. *Tanaka et al.* [1978] carried out measurements at scattering angles ranging from 15 to 130° and obtained the reported integral cross sections by extrapolation and integration of the measured differential cross sections. *Bromberg* [1970], *Du Bois and Rudd* [1976], and *Nickel et al.* [1988] measured the differential cross sections from 2 to 110°, 3 to 150°, and 20 to 120°, respectively but did not report integral cross sections. We extrapolated and integrated these differential cross sections. Q_{elas} values between 1 and 3 eV were obtained by extrapolation guided by the Q_T and Q_v results available in this region. We obtained Q_{elas} values between 20 and 100 eV by extrapolation and integration of the measured DCS [Nickel et al., 1988]. These results and the recommended values are shown in Figure 7.

Vibrational excitation cross sections are available for the $v=0$ to $v'=1$ excitation from *Ehrhardt et al.* [1968] and *Chutjian and Tanaka* [1980]. Cross sections for exciting higher vibrational levels are considerably smaller and since even the $v'=1$ excitation cross sections are very small compared to other cross sections, we neglected these contributions. The results and recommended values are shown in Figure 8.

Total ionization cross sections have been reported by *Asundi et al.* [1963], *Rapp and Englander-Golden* [1965] and *Orient and Srivastava* [1987]. The results of *Rapp and Englander-Golden* and *Orient and Srivastava* agree about 6%. We recommend the values obtained by *Rapp and Englander-Golden* [1965] since they are available over a wide energy range. These cross sections are shown in Figure 9.

A summary of the recommended cross sections and the calculated and recommended $\Sigma_n Q_{elec}^n$ values are given in Table 2 and in Figure 10. The $\Sigma_n Q_{elec}^n$ values obtained here are in good agreement with unpublished results of *Zetner et al.* [1988] excitation cross sections at 12.5 and 15 eV impact energies obtained for the sum of the $a^1\Pi$, $a^3\Sigma$, $d^3\Delta$ and $A^1\Pi$ states (which dominate the energy-loss spectra at these energies) plus a 20% estimated contributions from other states.

Methane

For CH_4 , total electron scattering cross sections are available from *Jones* [1985], *Ferch et al.* [1985], *Sucoka and Mori* [1986],

Lohmann and Buckman [1986], Dababneh et al. [1988], Nishimura and Sakae [1990], Zecca et al. [1991], Kanik et al. [1992b] and M. Hayashi (private communication, 1991). The agreement among these cross sections is, in general, within a few percent but the results of Sueoka and Mori [1986] and the recommended values of M. Hayashi (private communication, 1991) seem to be too low. They cannot be reconciled with other Q_T results with available Q_{elas} results. The total cross section values obtained by Dababneh et al. [1988] seem to be too high. These results and our recommended cross sections are shown in Figure 11.

Integral elastic scattering cross sections were derived from differential cross section measurements by Tanaka et al. [1982], Sakae et al. [1989] and Shyn and Cravens [1990]. M. Hayashi (unpublished data, 1991) made recommendations for these cross sections based on consistency checks. Curry et al. [1985] measured elastic scattering DCS for CH_4 in the 30 to 140° angular range at 7.5, 10, 12.5, 15, 17.5, and 20 eV impact energies. We extrapolated and integrated their results and obtained the corresponding Q_{elas} values. Sohn et al. [1986] measured elastic DCS in the 15 to 138° angular and 0.2 to 5 eV impact energy range. Again from these results, we calculated the corresponding integral cross sections. The values derived from DCS are in good agreement while the recommended values by Hayashi seem to be too small near the peak. The elastic cross sections do not converge to Q_T at low impact energies indicating errors, most likely in Q_{elas} , and/or large values for vibrational excitation cross sections. No Q_{elas} values are available below 3 eV. Figure 12 shows these results.

Cross sections for exciting the (v_1 and v_3) and (v_2 and v_4) unresolved vibrational modes have been determined from differential cross-sections measurements by Tanaka et al. [1982] and Shyn and Cravens (1991) and recommended by M. Hayashi (private communication, 1991). Curry et al. [1985] also measured DCS for excitation of the v_1 and v_3 unresolved and v_2 and v_4 unresolved vibrational modes in the 32.8 to 142.2° angular range at 7.5, 10, 12.5, 15, 17.5, and 20 eV impact energies. We extrapolated and integrated their results and obtained the integral vibrational excitation cross sections for the sum of these four fundamental modes. We show the cross section for the sum of these four fundamental mode excitations in Figure 13 together with our recommended values. The cross sections recommended by M. Hayashi (private communication, 1991) are much larger than our recommendation.

Total ionization cross sections for CH_4 are available from Tozer [1958], Rapp and Englander-Golden [1965], Peresse and Tuffin [1967], Chatham et al. [1984], Orient and Srivastava [1987] and Duric et al. [1991]. We judged, in agreement with M. Hayashi (private communication, 1991) that the most reliable cross sections over the widest energy range are those of Rapp and Englander-Golden [1965]. The ionization cross sections of Orient and Srivastava seem to be too large. If we use them in (1), we obtain negative values for $\sum_n Q_{\text{elec}}^n$. A summary of these cross sections is given in Figure 14.

The sum of all electronic excitation cross sections calculated by (1) from the recommended cross sections is shown in Figure 15 and compared to the same cross sections deduced from energy-loss spectra by Vuskovic and Trajmar [1983] and to the recommendations of M. Hayashi (private communication, 1991). The large values of the calculated total electronic excitation cross sections below about 10 eV (which is the threshold for electronic state excitation in CH_4) are obviously incorrect. They are due to the uncertainties in the Q_T but mainly in the Q_{elas} values. An error of 10% in these large cross sections could account for this artifact at low-impact energies. Additional uncertainties in the vibrational excitation cross sections could also contribute to this problem. We have information only on four fundamental modes. At a few eV impact energy other modes can have appreciable cross sections and resonance effects could greatly enhance vibrational excitation. We therefore based our recommendations on the results of Vuskovic and Trajmar [1983]. Since the electronic states of CH_4 are all dissociating (no discrete absorption or emission was observed for these states), the total electronic excitation cross sections should represent to a very good approximation the cross section for dissociation of CH_4 into neutral fragments. Dissociation to ionic species is included in the total ionization cross sections.

Summary of the recommended cross sections is given in Table 3 and Figure 16.

SUMMARY AND CONCLUSIONS

On the basis of independent measurements of the same cross sections and overall consistency of available data, we estimate that the recommended Q_T values are accurate to about 3 to 5%, the ionization cross sections to about 10 to 15%, and elastic scattering cross sections to about 10 to 30%. Vibrational excitation cross sections are likely accurate to about a factor of 2 but they do not significantly influence our derivations of $\sum_n Q_{\text{elec}}^n$ values. The derived $\sum_n Q_{\text{elec}}^n$ cross sections in general should be accurate to about 50%, which is not good but is the best we can do at the present time.

There is definitely need for more measurements to improve on the present situation. Refinement of Q_T values in the peak and lower impact energy regions would be desirable for all three molecules. There are more serious problems associated with elastic cross sections. Serious discrepancies exist among the limited data for O_2 and CO . These measurements should be repeated over the whole energy range. No measurements exist for CH_4 below 3 eV and O_2 below 2 eV.

Ionization cross sections could be improved, especially around 100 eV, where they have their peak value. The vibrational excitation cross sections are highly uncertain for CO and CH_4 and not available for O_2 , but fortunately, they are not important from the point of view of the deduction of total electronic state excitation cross sections.

We were able to derive only the sum of total electronic state and pure rovibrational state cross sections for O_2 and only in the threshold to 50 eV region. An estimation of the $\sum_n Q_{\text{elec}}^n$ values

from available electronic state excitation data is consistent with the derived ($\Sigma_n Q^n_{elec} + Q_v$) data, assuming that vibrational excitation is only a minor contribution.

For CO the $\Sigma_n Q^n_{elec}$ values derived here are in reasonably good agreement with the values obtained by summing the available electronic state excitations and estimating the missing contributions. For both of these diatomic molecules, only a fraction of electronic state excitations lead to dissociation to neutral fragments. The $\Sigma_n Q^n_{elec}$ values therefore represent an upper limit for Q_D .

In the case of CH₄, the $\Sigma_n Q^n_{elec}$ values cannot be reliably obtained from (1) because of the large uncertainties in Q_{elas} ; therefore, we based our recommendations on the measurements of Vuskovic and Trajmar [1983] at low-impact energies. At 200 eV the value obtained from (1) differs from their results only by about 35%. The cross sections recommended by M. Hayashi (personal communication, 1991) are about 35% higher than our recommendations.

Acknowledgments. The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology and was supported by the National Aeronautics and Space Administration under contract to the Jet Propulsion Laboratory. We also acknowledge support to one of us (S. T.) from the National Science Foundation.

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TABLE 1. Recommended Cross Sections for O₂

E_0 , eV	Q_T	Q_{elas}	Q_I	$\Sigma_n Q^n_{\text{elec}} + Q_V$		
				Calculated	<i>Trajmar et al.</i> [1971,1972]	recommended
1	5.80	5.80	0.00	0.00	0.00	0.000
2	6.20	6.20	0.00	0.00	0.00	0.000
3	6.60	6.60	0.00	0.00	0.00	0.000
4	6.90	6.80	0.00	0.10	0.075	0.100
5	7.40	7.30	0.00	0.10	0.082	0.100
6	8.06	7.90	0.00	0.16	----	0.160
7	8.70	8.30	0.00	0.40	0.11	0.400
8	9.09	8.60	0.00	0.49	----	0.490
9	10.15	8.80	0.00	1.35	----	1.350
10	10.38	8.90	0.00	1.48	0.30	1.480
12	10.76	9.10	0.00	1.66	----	1.660
15	10.70	9.00	0.07	1.63	1.48	1.630
20	10.75	8.60	0.29	1.86	1.06	1.860
30	11.10	7.80	0.81	2.49	----	2.490
40	10.71	7.10	1.36	2.25	1.78	2.250
50	10.28	6.50	1.82	1.96	----	1.960
60	9.78	6.10	2.17	1.51	----	1.510
70	9.46	5.70	2.46	1.30	----	1.300
80	9.19	5.40	2.67	1.12	----	1.120
90	8.98	5.00	2.81	1.17	----	1.170
100	8.67	4.80	2.91	0.96	----	0.960
200	6.10	3.15	2.75	0.20	----	0.200
300	4.85	2.40	2.33	0.12	----	0.120
400	4.00	2.00	1.98	0.02	----	0.020
500	3.50	1.72	1.71	0.07	----	0.070
600	3.10	1.53	1.52	0.05	----	0.050
700	2.80	1.37	1.36	0.07	----	0.070
800	2.55	1.27	1.23	0.05	----	0.050
900	2.35	1.18	1.12	0.05	----	0.050
1000	2.20	1.10	1.05	0.05	----	0.050

Electronic state excitation threshold is 0.98 eV; Ionization Potential = 12.06 eV. Values are in 10^{-16} cm^2 units.

TABLE 2. Recommended Cross Sections for CO

E_0 , eV	Q_T	Q_{elas}	Q_V	Q_I	$\Sigma_n Q^n_{\text{elec}}$	
					Calculated	Recommended
1	14.20	13.56	0.64	0.00	0.00	0.00
2	43.20	37.60	5.6	0.00	0.00	0.00
3	23.70	23.20	0.50	0.00	0.00	0.00
4	17.00	16.84	0.16	0.00	0.00	0.00
5	15.00	14.9	0.10	0.00	0.00	0.00
6	13.90	13.00	0.00	0.00	0.90	0.50
7	13.40	12.20	0.00	0.00	1.20	1.20
8	13.10	12.00	0.00	0.00	1.10	1.10
9	13.05	11.70	0.00	0.00	1.35	1.35
10	13.00	11.50	0.00	0.00	1.50	1.50
12	13.20	11.20	0.00	0.00	2.00	2.00
15	13.80	11.00	0.00	0.05	2.75	2.75
20	14.10	9.40	0.00	0.43	4.27	4.27
30	13.50	7.80	0.00	1.24	4.46	4.40
40	12.70	6.80	0.00	1.78	4.12	4.12
50	11.90	6.00	0.00	2.12	3.78	3.78
60	11.10	5.50	0.00	2.34	3.26	3.26
70	10.50	5.10	0.00	2.50	2.90	2.90
80	10.00	4.70	0.00	2.58	2.72	2.72
90	9.50	4.40	0.00	2.63	2.47	2.47
100	9.00	4.20	0.00	2.65	2.15	2.15
150	7.50	3.30	0.00	2.57	1.63	1.63
200	6.30	2.80	0.00	2.36	1.14	1.14
300	4.95	2.21	0.00	1.99	0.75	0.75
400	4.10	1.90	0.00	1.72	0.48	0.48
500	3.55	1.65	0.00	1.49	0.41	0.41
600	3.14	1.50	0.00	1.35	0.29	0.29
700	2.80	1.38	0.00	1.21	0.21	0.21
800	2.56	1.28	0.00	1.11	0.17	0.17
900	2.35	1.20	0.00	1.03	0.12	0.12
1000	2.18	1.10	0.00	0.958	0.12	0.12

Electronic state excitation threshold is 6.0 eV; Ionization Potential = 14.013 eV. Values are in 10^{-16} cm^2 units.

TABLE 3. Recommended Cross Sections for CH₄

E_0 , eV	Q_T	Q_{elas}	Q_V	Q_I	$\Sigma_n Q^n_{\text{elec}}$	
					Calculated	Recommended
1	2.40	1.65	0.42	0.00	0.33	0.00
2	6.25	4.35	0.42	0.00	1.48	0.00
3	10.00	7.40	0.44	0.00	2.16	0.00
4	14.60	11.00	0.63	0.00	2.97	0.00
5	19.80	14.70	0.80	0.00	4.30	0.00
6	23.25	17.00	0.95	0.00	5.30	0.00
7	25.00	19.00	1.27	0.00	4.73	0.00
8	25.70	19.80	1.09	0.00	4.81	0.00
9	25.20	20.00	0.88	0.00	4.32	0.00
10	24.80	19.40	0.75	0.00	4.65	0.27
12	23.60	18.20	0.55	0.00	4.85	0.65
15	21.10	16.90	0.39	0.20	3.61	1.12
20	18.60	14.80	0.30	1.20	2.30	1.75
30	15.40	11.35	0.21	2.37	1.47	1.75
40	13.50	8.70	0.17	3.02	1.61	1.42
50	12.00	6.80	0.14	3.36	1.70	1.20
60	11.00	5.80	0.125	3.56	1.52	1.01
70	10.20	5.30	0.103	3.66	1.13	0.90
80	9.55	5.00	0.105	3.69	0.76	0.80
90	9.40	4.70	0.10	3.99	0.61	0.74
100	8.80	4.50	0.10	3.66	0.54	0.67
150	7.00	3.30	----	3.30	0.40	0.47
200	5.97	2.66	----	2.99	0.32	0.37
300	4.50	1.90	----	2.47	0.13	0.26
400	3.70	1.50	----	2.08	0.12	0.21
500	3.10	1.23	----	1.82	0.05	0.17
600	2.72	1.07	----	1.63	0.02	0.15
700	2.47	0.95	----	1.47	0.05	0.13
800	2.26	0.85	----	1.34	0.07	0.12
900	2.09	0.77	----	1.24	0.08	0.11
1000	1.99	0.70	----	1.18	0.11	0.10

Electronic state excitation threshold is 9.0 eV; Ionization Potential = 12.6 eV. Values are in 10^{-16} cm^2 units.

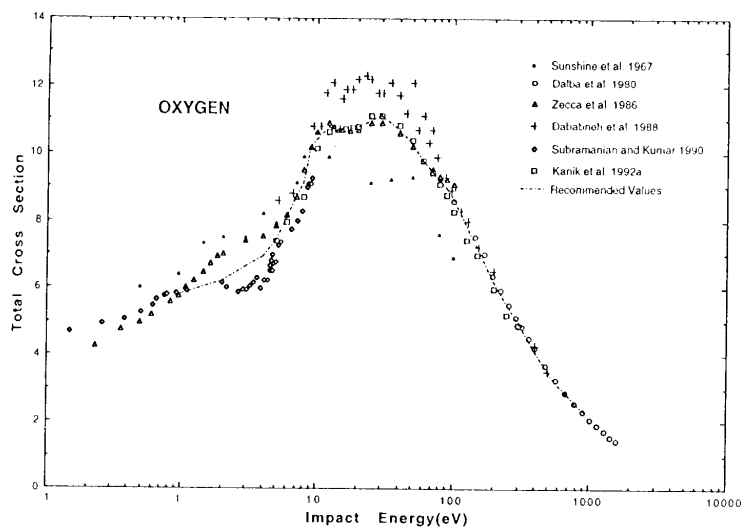


Fig. 1. Total electron scattering cross sections for O_2 . Dot-dash line refers to our recommended values in the 1 to 1000 eV region.

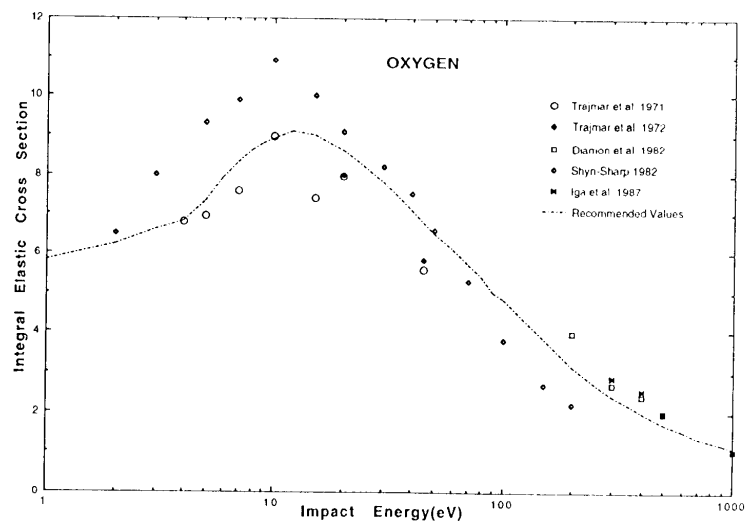


Fig. 2. Integral elastic scattering cross sections for O_2 . Dot-dash line refers to our recommended values in the 1 to 1000 eV region.

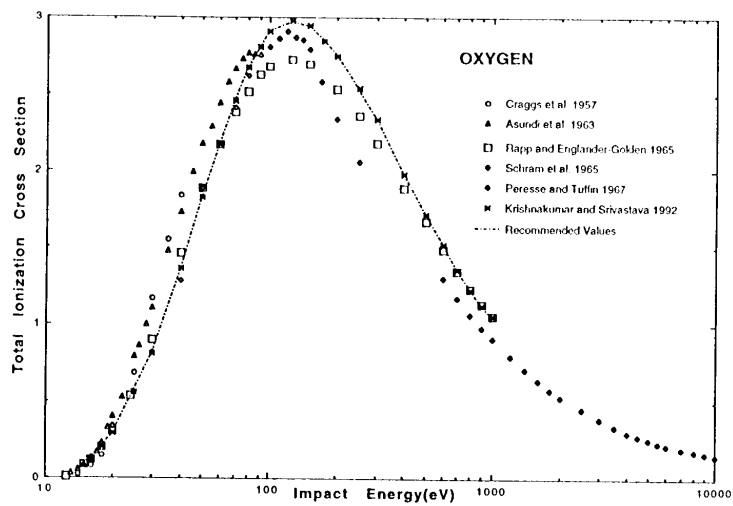


Fig. 3. Total ionization cross sections for O₂. Dot-dash curve represents the recommended values.

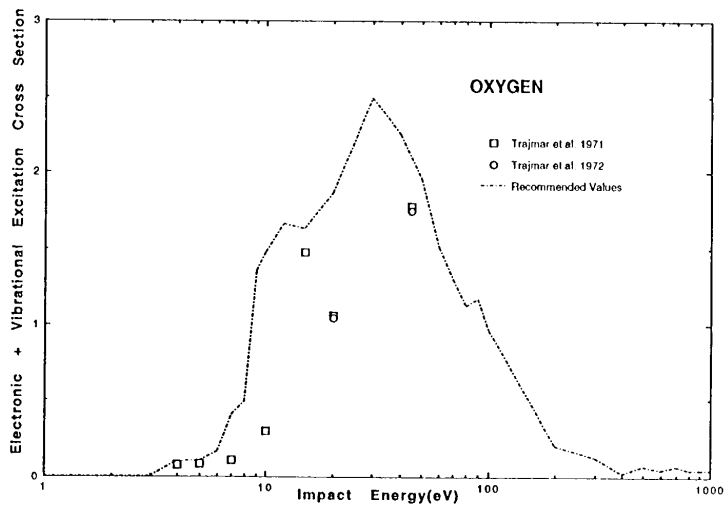


Fig. 4. Combined integral electronic state and pure vibrational state excitation cross sections for O₂. Recommended values are indicated by dot-dash line.

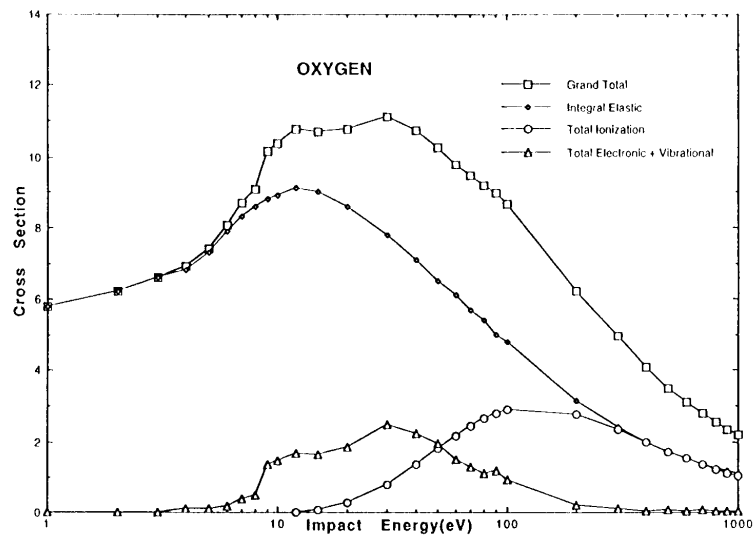


Fig. 5. Summary of recommended cross sections for O_2 in the 1 to 1000 eV range.

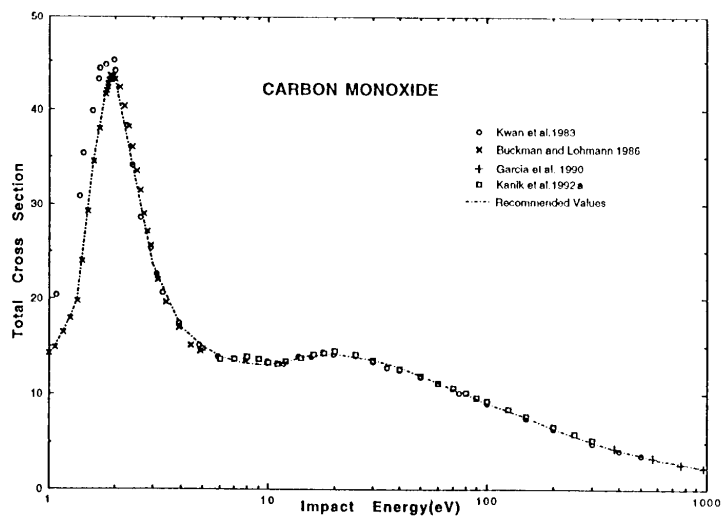


Fig. 6. Total electron scattering cross sections for CO. Dot-dash line represents the recommended cross sections.

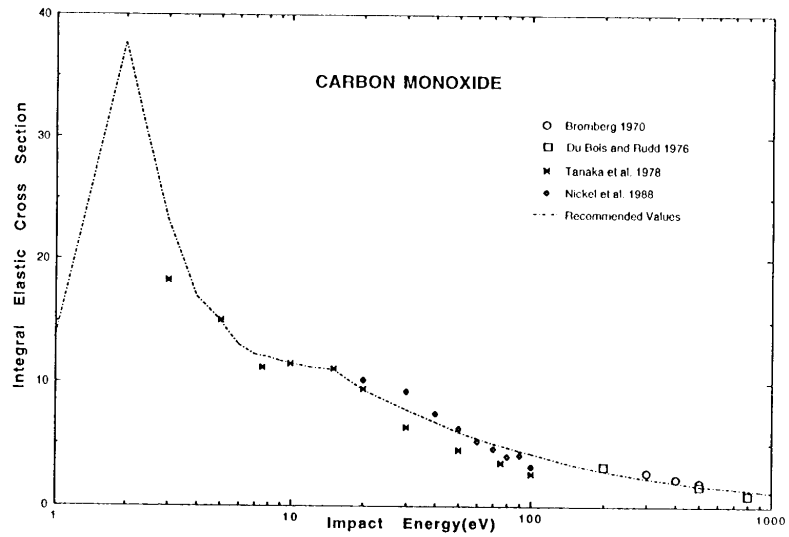


Fig. 7. Integral elastic scattering cross sections for CO. Recommended values are indicated by dot-dash line.

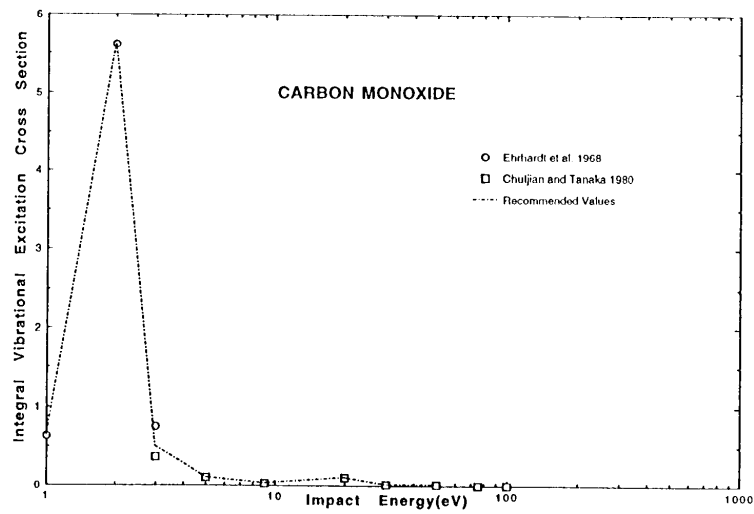


Fig. 8. Integral vibrational excitation cross sections for CO. Dot-dash line represents the recommended cross sections.

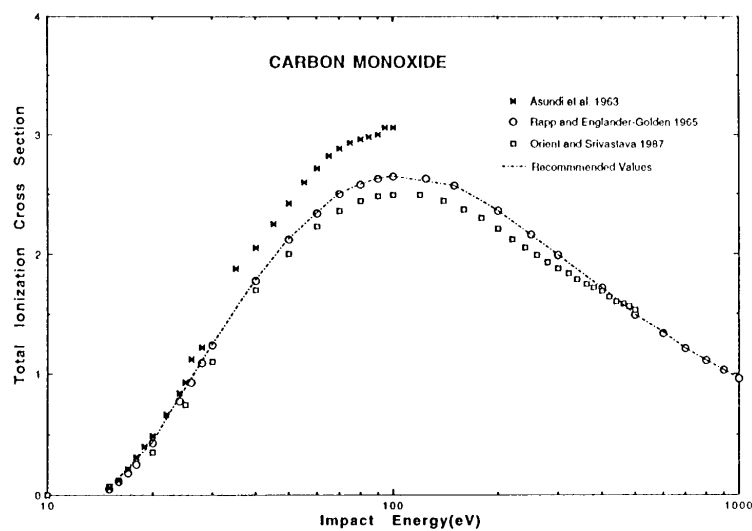


Fig. 9. Total ionization cross sections for CO. We selected the results of Rapp and Englander-Golden as our recommended cross sections.

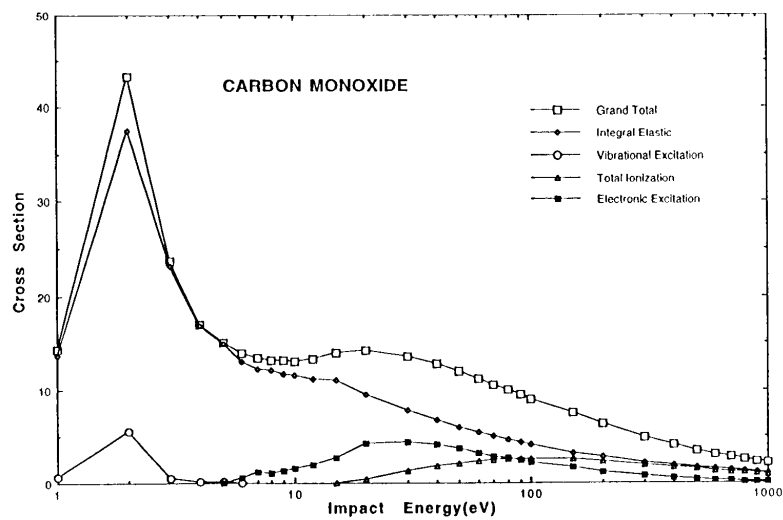


Fig. 10. Summary of recommended cross sections for CO in the 1 to 1000 eV impact energy range.

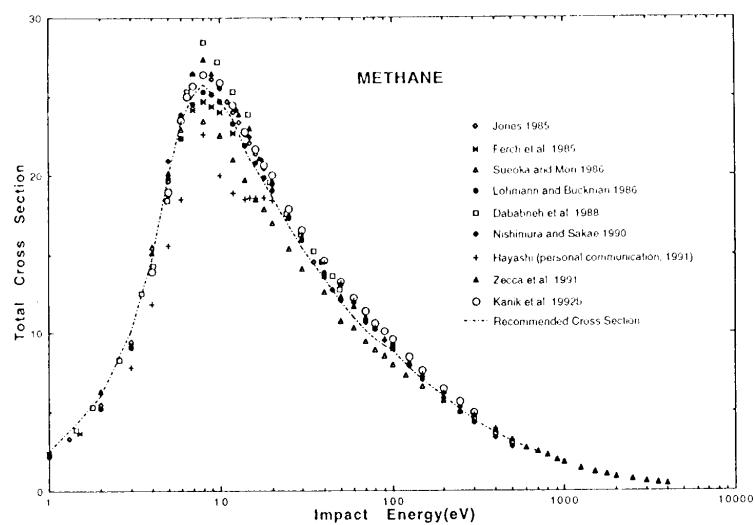


Fig. 11. Total electron scattering cross sections for CH_4 . The recommended values are represented by dot-dash line.

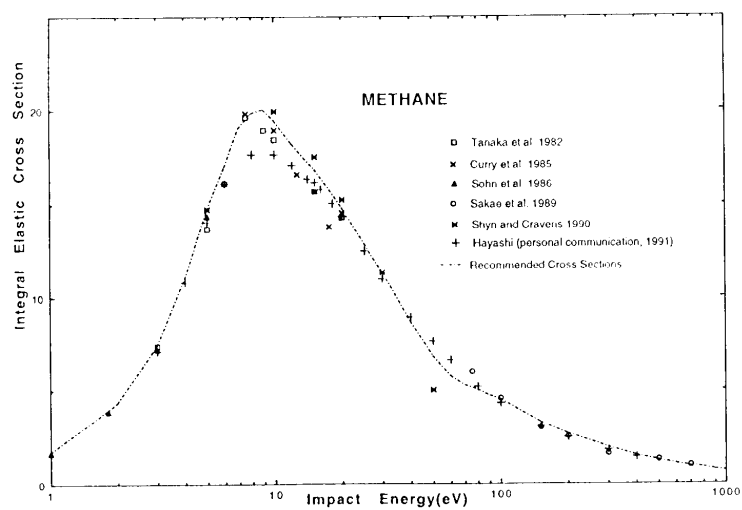


Fig. 12. Integral elastic cross sections for CH_4 . The dot-dash curve represents the recommended values.

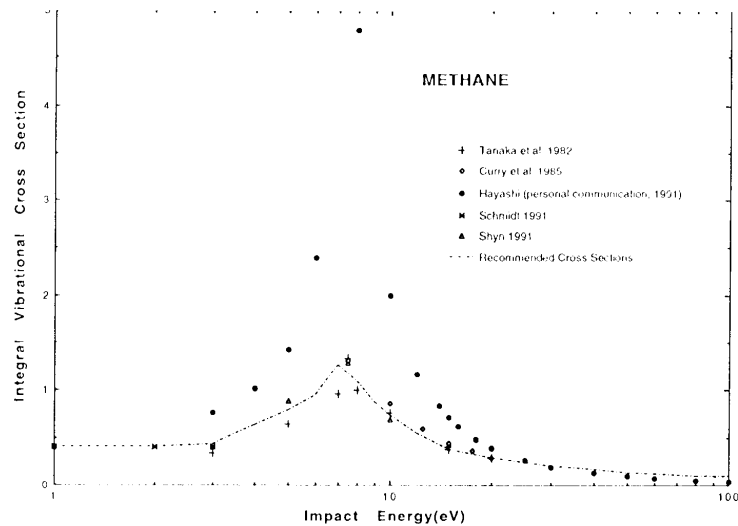


Fig. 13. Integral vibrational excitation cross sections for CH_4 . The recommended values are represented by dot-dash line.

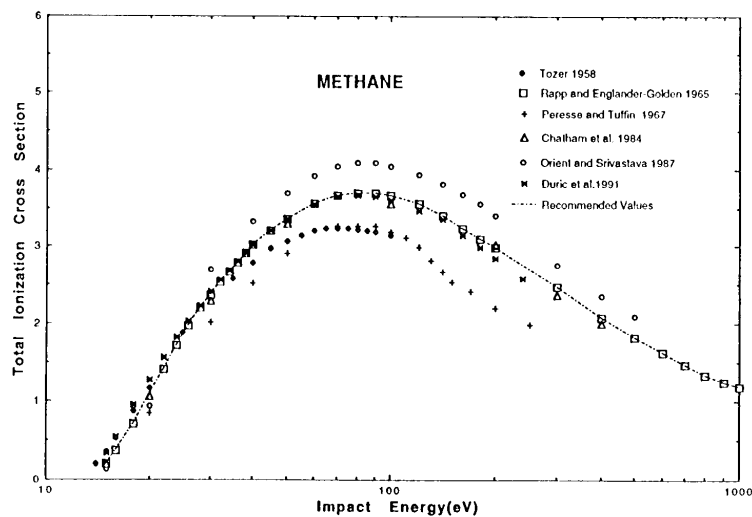


Fig. 14. Total ionization cross sections for CH_4 . We selected the results of Rapp and Englander-Golden as our recommended cross sections (dot-dash line).

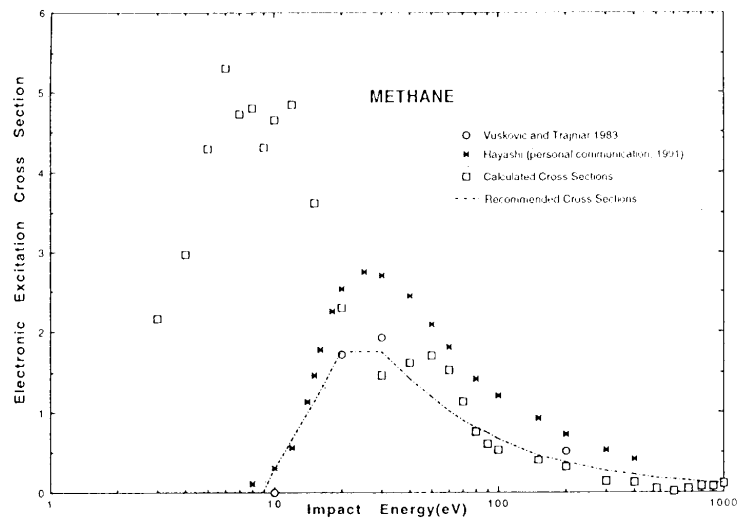


Fig. 15. Total electronic state excitation cross sections for CH_4 . The recommended values are represented by the dot-dash line.

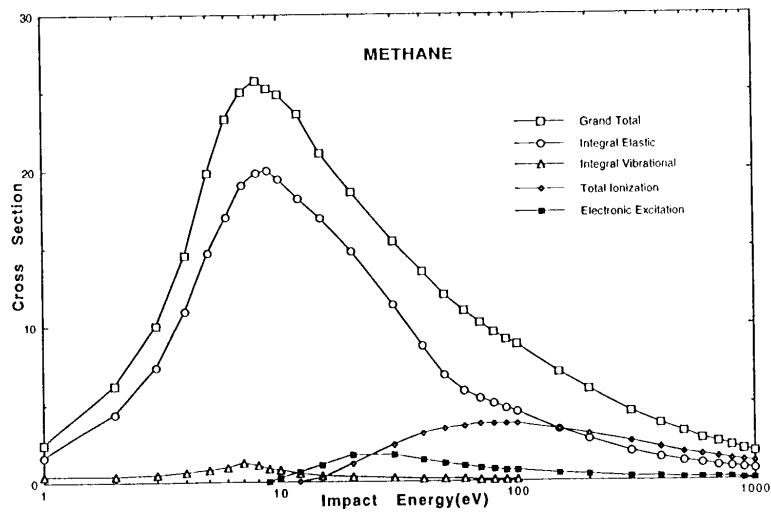


Fig. 16. Summary of recommended cross sections for CH_4 in the 1 to 1000 eV region.